mined by vpc and nmr analysis as above was 72:78. The assignments of the peaks in the vpc were verified by peak enhancement using the pure isomers from the preceding experiment.

(c) **From Olefinic Ketone.** In the same fashion a solution of 0.041 g (0.13 mmol) of the exocyclic methylene ketone **17** in 12 ml of freshly prepared polyphosphoric acid under a nitrogen atmosphere was allowed to stir at 60° (bath temperature) for 1.5 hr. The orange solution was cooled to room temperature and worked up as described above. The crude product (0.040 g) was again analyzed by vpc and nmr, and the two isomeric ketones **20** and **21** were found to be present in a ratio of 75:25. Again peak enhancement with samples of the pure isomers was used to verify assignments.

Stereochemistry of Low-Spin Iron Porphyrins. I. Bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) Chloride[1]

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Abstract. Bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride [written $(\mathrm{Im_2FeTPP})^+\mathrm{Cl}^-$] crystallizes as the 1:1 solvate from methanol solution. The monoclinic unit cell containing $4[(\mathrm{Im_2FeTPP})^+\mathrm{Cl}^-]\mathrm{CH_3OH}$ has a = 14.265, b = 16.390, and c = 18.121 Å, and β = 90.83° ($\bar{\lambda}$ = 1.54178 Å). Calculated and experimental densities are 1.367 and 1.36 g/ml, respectively, at 19°; the space group is $P2_1/n$. Measurement of diffracted intensities employed θ–2θ scanning with Cu Kα radiation on a four-circle diffractometer. Of the 6800 independent reflections scanned for $(\sin\theta)/\lambda < 0.562$ Å^{-1}, the 5299 retained as observed were used for the determination and anisotropic least-squares refinement of the 559 structural parameters; conventional and weighted R values of 0.076 and 0.077 were obtained. The octahedral $\mathrm{FeN_6}$ coordination group in the $(\mathrm{Im_2FeTPP})^+$ ion is dimensionally quasitetragonal. Equatorial Fe–N bond lengths are constrained by the porphinato core to the relatively high averaged value of 1.989 Å, with a mean deviation of 0.005 Å and an (individual) esd of 0.004 Å. Axial Fe–N bond lengths are 1.957 (4) and 1.991 (5) Å to, respectively, well-oriented and badly oriented imidazole ligands; the latter is strongly hydrogen bonded through its N–H group to the chloride ion, and is involved in substantial steric repulsions with porphinato nitrogen atoms. Stereochemical parameters of the porphinato core are consistent with the structural data from earlier and concurrent studies of iron porphyrins.

Inasmuch as each of the four possible combinations of ferrous(II) or ferric(III) iron in a *high*- or a *low*-spin ground state is realized in one or more of the naturally occurring iron porphyrins (the hemes in the hemoproteins), elucidation of the structural principles governing iron porphyrin stereochemistry carries many biologically significant implications. A five-coordinate square-pyramidal geometry, with the $\mathrm{Fe^{3+}}$ ion displaced ~0.50 Å out-of-plane from the porphinato core (see Figures 1 and 2 for diagrams of the porphinato skeleton), was established early as typical for the coordination group in a high-spin ferric porphyrin.[2,3] Explicit recognition of the pervasive role taken by the porphinato core in modulating the geometry of the coordination group, together with existing structural data for simpler iron complexes, led to the formulation of the overall pattern of iron porphyrin stereochemistry[3] that was freely employed for discussion of the anticipated configurational and conformational alterations attending the reversible oxygenation of the protohemes in hemoglobin and myoglobin.[3-6]

This stereochemical pattern[3] calls for square-pyramidal five-coordination in a high-spin ferrous porphyrin, with a substantially larger out-of-plane displacement of the $\mathrm{Fe^{2+}}$ ion than that of the smaller $\mathrm{Fe^{3+}}$ in a high-spin ferric porphyrin. It specifies further that addition to the five-coordinate high-spin iron ion, ferrous or ferric, of any sixth ligand effecting the transition to the low-spin state must bring the iron and the four porphinato nitrogen atoms into near or exact coplanarity with much shortened bonds.[7] It then led to the suggestion[4] that just such stereochemical alterations at a heme center accompanying the oxygenation of hemoglobin could require cooperative movements (translations and rotations of groups) in the protein framework, and thus provide a starting point for a mechanism to account for the cooperative interactions of the four subunits.[8]

Experimental confirmation of the proposed stereochemical pattern and of its direct applicability to the hemes in the hemoproteins has been delayed for about 5 years by untoward circumstances. Only recently have representative low-spin iron porphyrins, the bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride (written hereinafter as $(\mathrm{Im_2FeTPP})^+\mathrm{Cl}^-$)

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(2) D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965).

(3) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, **87**, 2312 (1965).

(4) J. L. Hoard in "Hemes and Hemoproteins," B. Chance, R. W. Estabrook, and T. Yonetani, Ed., Academic Press, New York, N. Y., 1966, pp 9–24.

(5) J. L. Hoard in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 573–594.

(6) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967).

(7) If, for the specific case of reversible oxygenation of the ferrous protoheme, the two atoms of the oxygen molecule are symmetrically attached to the iron atom (giving a sterically difficult seven-coordinate geometry), the iron atom should be displaced from the plane of the porphinato nitrogen atoms *toward* the oxygen molecule in order to achieve suitable overlap with the electron cloud of the latter.[3,5]

(8) J. Wyman, *Advan. Protein Chem.*, **19**, 223 (1964).

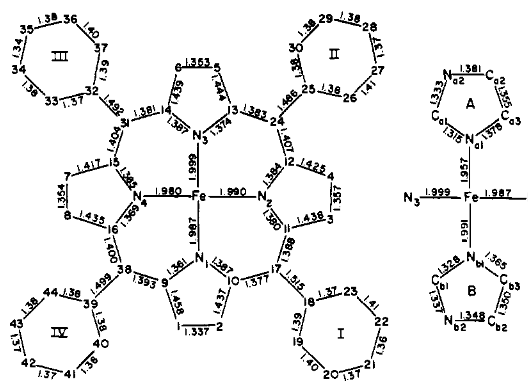

Figure 1. Formal diagrams showing the connexities of the arbitrarily numbered atoms and the bond lengths in, at left, the tetraphenylporphinatoiron(III) skeleton and, at right, the liganded imidazole skeletons. See Figures 2–4 for the detailed three-dimensional geometry of the $[Im_2FeTPP]^+$ ion.

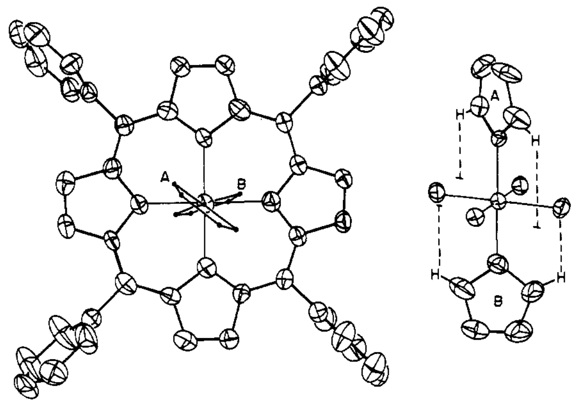

Figure 2. Computer-drawn models in perspective of, at left, the $[Im_2FeTPP]^+$ ion (with the thermal ellipsoids of the imidazole atoms suppressed) and, at right, the coordination group. The orientations of the imidazole ligands about the axial Fe–N bonds, qualitatively indicated in these diagrams, are quantitatively displayed in Figure 4.

treated in this paper[9] and the bis(piperidine)-α,β,γ,δ-tetraphenylporphinatoiron(II) (written Pip_2FeTPP) of the accompanying report,[10] yielded the single crystals that are essential to X-ray analyses of crystalline and molecular structures. The results obtained in both studies are in full agreement with expectation. But in apparently complete contradiction with the postulated pattern, the application of a form of Fourier difference synthesis in its *lowest* order of approximation to the X-ray data afforded by several pairings of quasiisomorphous hemoprotein derivatives had led the investigators[11] to conclude that the conformation of the heme, apart from the presence or absence of a ligand in the sixth position, is otherwise practically invariant to change in either the spin state or the oxidation state of the iron atom. The theoretical shortcomings of the zero-order difference synthesis are quite evident;[5] refinement of the complex phases for the derived quasiisomorphous structure is concomitant with a precise stereochemical description. Thus, by contrast, the recently reported data from hemoprotein structure analyses in which *ab initio* determination of the complex phases appropriate to each specific structure was employed lend their full support to the conclusion that the principles governing iron porphyrin stereochemistry are equally applicable to the protohemes in the hemoglobins. Love reports[12] that the low-spin carboxyhemoglobin and cyanomethemoglobin molecules from lamprey display the expected[3] centering of the respective Fe(II) and Fe(III) atoms within the hemes. Perutz now observes[13] that the high-spin five-coordinate ferrous ion is displaced ~0.75 Å out-of-plane in his deoxyhemoglobin structure. Perutz, indeed, has presented[13] a rather detailed structural model for the overall mechanism of reversible oxygenation in which the conformational change attending the oxygenation of a single heme initiates the cooperative interactions within the hemoglobin molecule.

A review of metalloporphyrin stereochemistry, with particular attention accorded to its applicability to the stereochemistry of hemes, has appeared elsewhere.[14]

Experimental Section

$(Im_2FeTPP)^+Cl^-$, prepared by the procedure of Epstein, *et al.*,[15] was obtained in crystalline form as the 1:1 solvate by recrystallization from methanol. Preliminary X-ray photographic study established a four-molecule unit with $P2_1/n$ as the uniquely probable space group utilized by the crystals. The largest crystal obtainable, an irregular prismatic fragment approximately 0.10 × 0.13 × 0.23 mm, was of good quality, displaying no sign of significant internal disorganization or crystal fracture. Precision lattice constants were obtained from a least-squares[16] treatment of the diffraction geometry based on angular settings for 43 reflections in the range $19° < |2\theta| < 61°$ ($\lambda = 1.54178$). These calculations yielded[17] $a = 14.265$ (3), $b = 16.390$ (4), $c = 18.121$ (5) Å, and cos $\beta = -0.0145$ (3) or $\beta = 90° 50'$. The setting data were obtained using the automatic centering program supplied with the computer-controlled diffractometer. Based on four solvated molecules in the unit cell the calculated density of 1.367 g/cm³ agreed well with the experimental value of 1.36 g/cm³ as obtained by flotation; all measurements were made at 19 ± 1°, the ambient laboratory temperature.

The preliminary investigation had shown that a maximum data–parameter ratio of ~10 could be achieved for the fully elaborated anisotropic model of the structure, hydrogen atoms excluded. Appraisal of the experimental alternatives led to the choice of Ni-filtered Cu $K\alpha$ radiation for the measurement of the diffracted intensities from the rather undersized crystal specified above. With this radiation and the geometrical limitations imposed by the diffractometer, the scanning of ~6800 independent reflections having $(\sin \theta)/\lambda < 0.562$ Å^{-1} at a fairly high level of sensitivity was permitted. The use of Mo $K\alpha$ radiation was rejected on the joint grounds of lowered sensitivity and the improbability that the measurements could be profitably extended to higher values of $(\sin \theta)/\lambda$. With the cited dimensions of the specimen crystal, its

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[9] See R. Countryman, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, **91**, 5166 (1969), for an earlier brief report.

[10] L. J. Radonovich, A. Bloom, and J. L. Hoard, *ibid.*, **94**, 2073 (1972).

[11] L. Stryer, J. C. Kendrew, and H. C. Watson, *J. Mol. Biol.*, **8**, 96 (1964); M. F. Perutz and F. S. Mathews, *ibid.*, **21**, 199 (1966); C. L. Nobbs, H. C. Watson, and J. C. Kendrew, *Nature* (*London*), **209**, 339 (1966). See also R. Huber, O. Epp, and H. Formanek, *J. Mol. Biol.*, **52**, 349 (1970), for a recent application of this approximate technique in which some part of the expected conformational changes in the hemes is observed.

[12] W. Love, *Proc. Int. Congr. Biochem., 8th*, 2 (1970); W. A. Hendrickson and W. E. Love, *Nature New Biol.*, **232**, 197 (1971).

[13] M. F. Perutz, *Nature* (*London*), **228**, 726, 734 (1970).

[14] J. L. Hoard, *Science*, **174**, 1295 (1971).

[15] L. M. Epstein, D. K. Straub, and C. Maricondi, *Inorg. Chem.*, **6**, 1721 (1967).

[16] Use was made of the Pick II computer program, a revision in this laboratory of W. C. Hamilton's Mode I program.

[17] The equivalent description which meets Donnay's lattice parameter criteria[18] and utilizes space group $P2_1/a$[19] has $a = 23.224$, $b = 16.390$, and $c = 14.265$ Å, and cos $\beta = -0.6255$ or $\beta = 128° 43'$.

[18] J. D. H. Donnay, Ed., "Crystal Data," 2nd ed, American Crystallographic Association, New York, N. Y., 1963.

[19] N. F. M. Henry and K. Lonsdale, Ed., "International Tables for X-ray Crystallography, Vol. I. Symmetry Groups," 2nd ed, The Kynoch Press, Birmingham, England, 1965.

mounting with the shortest dimension approximately parallel to the rotation axis of the goniometer head, and a linear absorption coefficient of 3.9 mm^{-1} for Cu Kα radiation, the maximum error in any structure factor occasioned by the neglect of absorption corrections was estimated to be ~6%. The irregularities in the shape of the crystal precluded the accurate calculation of absorption corrections except by computations of prohibitive cost.[20]

Diffracted intensities were automatically measured at a take-off angle of ~2° using the θ–2θ scanning technique. The range of each scan, taken at 1°/min, consisted of the generously estimated reflection base width of 2.0° at $2\theta = 0$ and an increment,[22] $\Delta(2\theta) = (0.285 \tan \theta)°$, to allow for spectral dispersion; background counts of 40-sec duration were taken at both limits of the scan. The intensities of three standard reflections monitored at intervals of 250 data points betrayed no secular trend.

The net intensities were reduced to relative squared amplitudes, $|F_o|^2$, by means of the standard Lorentz and polarization factor (Lp). Those reflections retained as observed data satisfied the criterion $|F_o| > 0.50\sigma_F$, wherein σ_F is the standard deviation computed from $\sigma_F{}^2 = (Ct + k^2B)/4|F_o|^2(Lp)^2$, Ct being the total count from the scan, k the ratio of scanning time to total background counting time, and B the total background count. This rejection level was established to ensure retention of all reflections objectively observed as visible peaks on a strip-chart recorder while excluding all formally negative, and an approximately equal number of formally positive, intensities. Thus, the set of unique reflections employed for the determination and refinement of structure comprised 5299 observed data.

Analysis of a three-dimensional Patterson synthesis of the $|F_o|^2$ data led to placement of the iron atoms in general positions of the space group.[19] The remaining structure, save hydrogen atoms, was developed by means of Fourier and difference syntheses in which the initial phases associated with the structure-factor moduli were based on the calculated contributions from the iron atoms. Initial refinement of coordinates and isotropic thermal parameters of the 62 atoms (hydrogen excluded) in the asymmetric unit employed block-diagonal[23] least-squares minimization[24] of the function, $\Sigma w(|F_o| - |F_c|)^2$. A difference synthesis then revealed concentrations of electron density at the approximate positions chemically anticipated for all hydrogen atoms excepting those of the methanol solvate; these observed positions were adjusted to give apparent C–H and N–H bond distances of 0.98 Å and were not varied during further refinement.[25] Converging cycles of least-squares refinement, with $w = 1$, of the 559 parameters describing the anisotropic structural model (the assigned isotropic thermal parameters of the hydrogen atoms were not varied) led to a conventional R of 0.076 and a weighted residual of 0.077 for the data–parameter ratio of 9.5. Examination of a smoothed, slowly varying, empirical weighting function of the type described earlier[23] showed that it departed significantly from unity only for the very largest and smallest structure factors. Experience with other metalloporphyrin structure determinations[21,23] strongly suggests that bond parameters within the porphinato core and the coordination group are insensitive to the point of practical invariance to rather substantial alterations in the weighting scheme.[26] Consequently, the costly additional computations required for introduction of the somewhat modified weighting scheme were not performed. A final difference synthesis having a maximum electron density of 0.5 e/Å^3 was adjudged to be free of significant features.[27]

Table I. Atomic Coordinates in the Unit Cell

Atom type	Coordinates with standard deviations^a 10^4x	10^4y	10^4z
Fe^b	1951 (1)	6454 (0)	3951 (0)
N_1	2267 (3)	5414 (3)	3450 (2)
N_2	2521 (3)	6044 (3)	4889 (2)
N_3	1608 (3)	7493 (3)	4459 (2)
N_4	1381 (3)	6865 (3)	3020 (2)
C_1	2521 (5)	4426 (3)	2574 (3)
C_2	2774 (4)	4101 (3)	3223 (3)
C_3	3259 (5)	5231 (4)	5756 (3)
C_4	3139 (4)	5976 (4)	6069 (3)
C_5	1380 (5)	8476 (4)	5349 (3)
C_6	829 (5)	8672 (4)	4761 (3)
C_7	534 (4)	7618 (3)	2184 (3)
C_8	946 (4)	7011 (3)	1799 (3)
C_9	2200 (4)	5255 (3)	2714 (3)
C_{10}	2641 (4)	4718 (3)	3776 (3)
C_{11}	2885 (4)	5275 (3)	5016 (3)
C_{12}	2680 (4)	6479 (3)	5533 (3)
C_{13}	1846 (4)	7722 (3)	5167 (3)
C_{14}	980 (4)	8072 (3)	4195 (3)
C_{15}	809 (4)	7542 (3)	2935 (3)
C_{16}	1452 (4)	6528 (3)	2332 (3)
C_{17}	2921 (4)	4648 (3)	4503 (3)
C_{18}	3376 (4)	3856 (3)	4751 (3)
C_{19}	2860 (5)	3228 (4)	5036 (4)
C_{20}	3296 (6)	2493 (4)	5257 (4)
C_{21}	4240 (6)	2411 (4)	5194 (4)
C_{22}	4772 (5)	3032 (5)	4916 (4)
C_{23}	4341 (5)	3760 (4)	4685 (4)
C_{24}	2383 (4)	7283 (3)	5668 (3)
C_{25}	2603 (4)	7659 (3)	6396 (3)
C_{26}	3295 (4)	8247 (4)	6461 (4)
C_{27}	3467 (5)	8626 (4)	7146 (5)
C_{28}	2948 (6)	8417 (5)	7745 (4)
C_{29}	2264 (5)	7824 (5)	7686 (4)
C_{30}	2091 (5)	7454 (4)	7012 (3)
C_{31}	582 (4)	8096 (3)	3496 (3)
C_{32}	−107 (4)	8757 (3)	3325 (3)
C_{33}	−1047 (5)	8587 (5)	3295 (5)
C_{34}	−1693 (6)	9189 (6)	3133 (5)
C_{35}	−1422 (6)	9961 (6)	3010 (4)
C_{36}	−478 (7)	10158 (5)	3047 (6)
C_{37}	189 (5)	9550 (4)	3201 (5)
C_{38}	1871 (4)	5780 (3)	2164 (3)
C_{39}	1917 (4)	5528 (3)	1370 (3)
C_{40}	2688 (5)	5748 (4)	962 (4)
C_{41}	2748 (6)	5531 (5)	230 (4)
C_{42}	2030 (7)	5111 (5)	−109 (4)
C_{43}	1268 (7)	4881 (5)	290 (4)
C_{44}	1210 (6)	5095 (5)	1027 (4)
N_{a1}	718 (3)	6021 (3)	4206 (2)
N_{a2}	−566 (4)	5808 (4)	4827 (4)
C_{a1}	278 (4)	6158 (4)	4826 (4)
C_{a2}	−671 (5)	5427 (4)	4152 (4)
C_{a3}	126 (5)	5554 (4)	3771 (4)
N_{b1}	3187 (3)	6896 (3)	3650 (3)
N_{b2}	4273 (4)	7760 (4)	3326 (3)
C_{b1}	3419 (4)	7680 (4)	3612 (4)
C_{b2}	4608 (5)	7006 (5)	3193 (4)
C_{b3}	3941 (4)	6472 (4)	3400 (4)
Cl	496 (1)	5865 (1)	7713 (1)
$O_m{}^c$	−612 (5)	6491 (4)	6303 (3)
$C_m{}^c$	−789 (10)	7331 (6)	6346 (6)

^{a} Numbers in parentheses are the estimated standard deviations. ^{b} For Fe, $10^5x = 19505$ (6), $10^5y = 64544$ (5), and $10^5z = 39512$ (4). ^{c} Symbols for atoms in a methanol solvate molecule.

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(20) That the apparent positions of the atoms (hydrogen excluded) are trivially affected by neglecting absorption corrections of this magnitude is strongly supported by a concurrent structure determination for excellent crystals of $\alpha,\beta,\gamma,\delta$-tetraphenylporphinatodichlorotin(IV).[21]

(21) D. M. Collins, W. R. Scheidt, and J. L. Hoard, submitted to *J. Amer. Chem. Soc.*

(22) T. C. Furnas, "Single Crystal Orienter Instruction Manual," The General Electric Company, Milwaukee, Wis., 1966, p 79.

(23) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970).

(24) Atomic form factors from D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968), with corrections, real and imaginary, for the anomalous scattering of the iron atom from D. T. Cromer, *ibid.*, **18**, 17 (1965), were used in least-squares refinement of the structural parameters.

(25) The atomic form factor used for hydrogen was from: C. H. MacGillavry, G. D. Rieck, and K. Lonsdale, Ed., "International Tables for X-ray Crystallography, Vol. III. Physical and Chemical Tables," 2nd ed, The Kynoch Press, Birmingham, England, 1968.

(26) Apparent bond parameters in phenyl[21] or 4-pyridyl[23] groups that are peripherally attached to the porphine skeleton are rather more sensitive to change in the weighting scheme. Even in the most favorable case, the treatment of these peripheral groups demands a more sophisticated model than any that is commonly in vogue.

(27) A table of the 5299 observed and calculated amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to

Table II. Thermal Parameters of the Atoms in the Crystals

Atom type	Anisotropic parameters (A^2) with standard deviations[a]						
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B[b]
Fe	2.26 (3)	1.91 (3)	2.80 (3)	0.06 (3)	0.16 (3)	0.00 (3)	2.29
N_1	2.4 (2)	2.4 (2)	3.0 (2)	0.2 (2)	0.1 (1)	−0.3 (2)	2.5
N_2	2.6 (2)	2.1 (2)	3.0 (2)	0.2 (2)	0.0 (1)	0.0 (2)	2.5
N_3	3.2 (2)	1.9 (2)	3.0 (2)	0.5 (2)	0.1 (2)	0.0 (2)	2.6
N_4	2.6 (2)	2.2 (2)	2.8 (2)	0.1 (2)	0.1 (1)	0.1 (2)	2.5
C_1	4.1 (3)	2.6 (2)	3.4 (3)	0.6 (2)	0.6 (2)	−0.6 (2)	3.2
C_2	3.7 (3)	2.4 (2)	3.8 (3)	0.9 (2)	−0.2 (2)	−0.3 (2)	3.1
C_3	4.4 (3)	3.1 (3)	3.5 (3)	0.6 (2)	0.1 (2)	0.4 (2)	3.6
C_4	3.8 (3)	3.6 (3)	3.3 (3)	0.9 (2)	−0.2 (2)	0.0 (2)	3.5
C_5	4.9 (3)	2.7 (3)	4.1 (3)	0.3 (2)	−0.3 (3)	−1.0 (2)	3.6
C_6	4.5 (3)	2.6 (3)	4.3 (3)	1.2 (2)	−0.2 (3)	−0.9 (2)	3.4
C_7	2.9 (3)	2.9 (3)	3.6 (3)	0.1 (2)	−0.3 (2)	0.5 (2)	3.1
C_8	3.9 (3)	2.6 (2)	3.2 (3)	−0.2 (2)	−0.3 (2)	−0.1 (2)	3.2
C_9	2.1 (2)	2.2 (2)	3.6 (3)	−0.1 (2)	0.2 (2)	−0.1 (2)	2.6
C_{10}	2.5 (2)	2.4 (2)	3.2 (3)	0.0 (2)	0.7 (2)	0.1 (2)	2.6
C_{11}	2.1 (2)	2.7 (2)	3.7 (3)	0.3 (2)	0.1 (2)	0.4 (2)	2.7
C_{12}	2.8 (2)	2.9 (3)	2.8 (2)	0.2 (2)	−0.1 (2)	0.0 (2)	2.8
C_{13}	3.9 (3)	2.3 (2)	3.3 (3)	−0.5 (2)	−0.2 (2)	−0.3 (2)	3.0
C_{14}	3.1 (3)	1.8 (2)	3.6 (3)	0.4 (2)	0.4 (2)	0.1 (2)	2.7
C_{15}	2.1 (2)	2.6 (2)	2.9 (2)	−0.1 (2)	−0.0 (2)	0.5 (2)	2.5
C_{16}	2.9 (3)	2.5 (2)	2.4 (2)	−0.3 (2)	0.3 (2)	0.0 (2)	2.6
C_{17}	2.8 (2)	2.2 (2)	3.4 (3)	0.3 (3)	0.2 (2)	−0.2 (2)	2.7
C_{18}	3.3 (3)	2.4 (2)	3.3 (3)	0.8 (2)	−0.1 (2)	−0.3 (2)	2.9
C_{19}	4.0 (3)	3.9 (3)	5.5 (4)	1.0 (3)	−0.5 (3)	0.0 (4)	4.3
C_{20}	4.4 (5)	5.4 (3)	6.6 (4)	2.1 (3)	−1.6 (4)	−0.2 (3)	4.9
C_{21}	7.4 (5)	3.6 (3)	4.7 (4)	2.3 (3)	−2.2 (3)	−0.4 (3)	4.4
C_{22}	7.8 (4)	2.9 (4)	6.3 (4)	1.0 (3)	0.2 (3)	1.2 (3)	5.0
C_{23}	4.4 (3)	2.8 (3)	6.7 (4)	0.4 (3)	0.4 (3)	0.9 (3)	4.2
C_{24}	2.9 (3)	2.7 (2)	3.3 (3)	−0.2 (2)	0.1 (2)	−0.1 (2)	2.9
C_{25}	3.1 (3)	2.8 (3)	3.9 (3)	0.8 (2)	−1.1 (2)	−0.8 (2)	3.0
C_{26}	3.5 (3)	3.5 (3)	5.3 (4)	0.2 (2)	−0.8 (3)	−0.8 (3)	3.9
C_{27}	4.0 (3)	4.2 (3)	8.3 (5)	0.4 (3)	−2.1 (3)	−2.2 (3)	4.7
C_{28}	6.4 (4)	4.7 (4)	5.9 (4)	2.2 (3)	−1.8 (3)	−1.8 (3)	5.0
C_{29}	5.2 (4)	5.4 (4)	4.6 (3)	1.9 (3)	−0.4 (3)	0.0 (3)	4.8
C_{30}	4.3 (3)	4.6 (3)	2.9 (3)	0.5 (3)	−0.3 (2)	−0.4 (2)	3.8
C_{31}	2.8 (3)	2.5 (2)	3.7 (3)	0.2 (2)	0.2 (2)	0.5 (2)	2.9
C_{32}	3.9 (2)	3.0 (3)	3.0 (3)	1.2 (2)	0.1 (2)	0.3 (2)	3.1
C_{33}	3.6 (3)	4.9 (4)	7.6 (5)	1.5 (3)	−0.7 (3)	−1.4 (3)	4.8
C_{34}	5.4 (4)	7.7 (5)	7.0 (5)	3.0 (4)	−2.4 (4)	−2.5 (4)	5.7
C_{35}	7.8 (5)	8.7 (6)	4.7 (4)	6.4 (5)	−0.2 (4)	−0.3 (4)	5.0
C_{36}	10.2 (7)	4.4 (4)	10.0 (6)	4.0 (4)	3.2 (5)	2.5 (4)	6.3
C_{37}	5.2 (4)	3.8 (3)	9.3 (5)	1.9 (3)	2.9 (4)	2.8 (3)	4.8
C_{38}	2.9 (3)	2.6 (2)	3.3 (3)	−0.2 (2)	0.4 (2)	−0.4 (2)	2.9
C_{39}	4.4 (3)	2.6 (2)	3.2 (3)	0.4 (2)	0.1 (2)	0.0 (2)	3.3
C_{40}	5.7 (4)	5.0 (3)	4.8 (3)	−1.1 (3)	0.2 (3)	−1.7 (3)	4.9
C_{41}	8.3 (4)	5.6 (4)	4.8 (4)	−0.1 (3)	−0.8 (3)	−2.3 (3)	5.6
C_{42}	9.5 (6)	4.7 (4)	3.9 (3)	1.7 (4)	1.1 (4)	−0.6 (3)	5.4
C_{43}	6.8 (5)	5.4 (4)	4.8 (4)	1.0 (4)	2.4 (4)	0.3 (3)	5.2
C_{44}	4.9 (4)	4.5 (4)	4.3 (4)	0.7 (3)	0.9 (3)	0.3 (3)	4.5
N_{a1}	2.3 (2)	2.6 (2)	3.3 (2)	0.4 (2)	0.5 (1)	0.6 (2)	2.6
N_{a2}	3.7 (3)	5.2 (3)	7.6 (4)	1.3 (2)	1.9 (3)	1.6 (3)	4.8
C_{a1}	3.5 (3)	2.9 (3)	5.8 (4)	0.5 (2)	1.3 (3)	0.6 (3)	3.7
C_{a2}	2.9 (3)	4.6 (3)	7.6 (4)	−1.6 (3)	−0.8 (3)	2.7 (3)	4.0
C_{a3}	4.2 (3)	4.0 (3)	5.0 (3)	−1.0 (3)	−0.8 (3)	1.4 (3)	4.1
N_{b1}	2.7 (2)	2.8 (2)	3.7 (2)	−0.5 (2)	−0.1 (2)	0.3 (2)	3.0
N_{b2}	4.5 (3)	4.8 (3)	4.8 (3)	−2.2 (2)	0.5 (2)	0.6 (2)	4.3
C_{b1}	3.6 (3)	3.2 (3)	5.0 (3)	−0.8 (2)	0.1 (3)	1.1 (2)	3.7
C_{b2}	3.7 (3)	5.6 (4)	7.3 (4)	−1.7 (3)	1.5 (3)	−1.2 (3)	4.9
C_{b3}	3.3 (3)	4.0 (3)	6.1 (4)	−0.7 (3)	1.2 (3)	−1.3 (3)	4.1
Cl	5.15 (9)	3.95 (8)	8.59 (10)	0.53 (7)	1.71 (9)	−0.76 (8)	5.39
O_m[c]	10.9 (5)	7.8 (4)	6.9 (3)	1.0 (3)	2.1 (3)	−1.4 (3)	8.0
C_m[c]	15.2 (10)	6.4 (5)	8.4 (6)	1.3 (6)	0.1 (7)	−0.8 (5)	9.3

[a] Numbers in parentheses are the estimated standard deviations. B_{ij} is related to the dimensionless β_{ij} employed during refinement as $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Isotropic thermal parameters as calculated from $B = 4[V^2\det(\beta_{ij})]^{1/3}$. [c] Symbols for atoms in a methanol solvate molecule.

Atomic coordinates and the associated anisotropic thermal parameters describing the crystalline arrangement are listed in Tables I and II, respectively. The numbering of the atoms in Figure 1 is maintained in Tables I–V.

Discussion

Tables III and IV are listings of the bond lengths and bond angles, respectively, in the coordination group, porphinato skeleton, and imidazole rings of the (Im_2-FeTPP)$^+$ cation; Table V is a listing of the mostly less precise and less interesting data associated with the

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Table III. Bond Lengths in the Coordination Group, Porphinato Skeleton, and Imidazole Rings[a]

Type	Length, Å	Type	Length, Å	Type	Length, Å
$Fe-N_1$	1.987 (4)	C_1-C_9	1.458 (8)	$C_{13}-C_{24}$	1.383 (8)
$Fe-N_2$	1.990 (4)	C_2-C_{10}	1.437 (8)	$C_{14}-C_{31}$	1.381 (8)
$Fe-N_3$	1.999 (4)	C_3-C_4	1.357 (9)	$C_{15}-C_{31}$	1.404 (8)
$Fe-N_4$	1.980 (4)	C_3-C_{11}	1.438 (8)	$C_{16}-C_{38}$	1.400 (8)
$Fe-N_{a1}$	1.957 (4)	C_4-C_{12}	1.425 (8)	$N_{a1}-C_{a1}$	1.315 (8)
$Fe-N_{b1}$	1.991 (5)	C_5-C_6	1.353 (9)	$N_{a1}-C_{a3}$	1.378 (8)
N_1-C_9	1.361 (7)	C_5-C_{13}	1.444 (8)	$N_{a2}-C_{a1}$	1.333 (9)
N_1-C_{10}	1.387 (7)	C_6-C_{14}	1.439 (8)	$N_{a2}-C_{a2}$	1.381 (11)
N_2-C_{11}	1.380 (7)	C_7-C_8	1.354 (8)	$C_{a2}-C_{a3}$	1.355 (10)
N_2-C_{12}	1.384 (7)	C_7-C_{15}	1.417 (8)	$N_{b1}-C_{b1}$	1.328 (8)
N_3-C_{13}	1.374 (7)	C_8-C_{16}	1.435 (8)	$N_{b1}-C_{b3}$	1.365 (8)
N_3-C_{14}	1.387 (7)	C_9-C_{38}	1.393 (8)	$N_{b2}-C_{b1}$	1.337 (8)
N_4-C_{15}	1.385 (7)	$C_{10}-C_{17}$	1.377 (8)	$N_{b2}-C_{b2}$	1.348 (10)
N_4-C_{16}	1.369 (7)	$C_{11}-C_{17}$	1.388 (8)	$C_{b2}-C_{b3}$	1.350 (9)
C_1-C_2	1.337 (8)	$C_{12}-C_{24}$	1.407 (8)		

[a] Numbers in parentheses are the estimated standard deviations.

peripheral phenyl groups and the methanol of solvation. The configuration of the $(Im_2FeTPP)^+$ cation, of no required symmetry as it exists in the crystal, is illustrated in the computer-drawn diagrams of Figure 2; the effective symmetry of the complex is of immediate interest.

A quantitative description of the rather pronounced quasi-S_4 ruffling of the porphinato skeleton is provided by Figure 3; the numbered atomic symbols in the porphinato core of Figure 1 are replaced in Figure 3 by the displacements (in units of 0.01 Å) of the corresponding atoms from the mean skeletal plane. In magnitude and kind, the observed ruffling is reminiscent of that observed in tetragonal crystals of tetraphenylporphine[28] and its copper(II) and palladium(II) derivatives.[29] As is usual, local flatness (within 0.02 Å) of the pyrrole rings and of the trigonal bond patterns emanating from the carbon atoms in the inner 16-membered ring is preserved.[23,28] The unremarkable character of the skeletal ruffling is suggested by the circumstance that there is currently just one authenticated example of a crystalline porphyrin in which the porphinato core seems unambiguously to be planar.[21]

The angles made by the planes of the peripheral phenyl groups I–IV (Figures 1 and 2) with the mean plane of the porphinato core are 88.6, 76.8, 76.0, and 88.1°, respectively. Angles smaller than ~60° presumably are precluded by steric interactions between contiguous pyrrole hydrogen and phenyl hydrogen atoms. The averaged length of the four chemically similar, but structurally nonequivalent, bonds connecting phenyl carbon with methine carbon atoms (Table V) is 1.498 (5, 8) Å, wherein the first figure in parentheses is the mean deviation (in units of 0.001 Å) from the average and the second is the root-mean-

Table IV. Bond Angles in the Coordination Group, Porphinato Skeleton, and Imidazole Rings[a]

Angle	Value, deg	Angle	Value, deg	Angle	Value, deg
N_1FeN_2	90.4 (2)	$C_1C_2C_{10}$	107.2 (5)	$N_4C_{15}C_7$	109.4 (5)
N_1FeN_4	89.8 (2)	$C_4C_3C_{11}$	107.3 (5)	$N_4C_{15}C_{31}$	125.3 (5)
N_1FeN_{a1}	90.4 (2)	$C_3C_4C_{12}$	107.1 (5)	$C_7C_{15}C_{31}$	125.2 (5)
N_1FeN_{b1}	88.8 (2)	$C_6C_5C_{13}$	106.7 (5)	$N_4C_{16}C_8$	110.4 (5)
N_2FeN_3	89.7 (2)	$C_5C_6C_{14}$	107.9 (5)	$N_4C_{16}C_{38}$	126.1 (5)
N_2FeN_{a1}	91.9 (2)	$C_8C_7C_{15}$	108.3 (5)	$C_8C_{16}C_{38}$	123.3 (5)
N_2FeN_{b1}	90.2 (2)	$C_7C_8C_{16}$	106.0 (5)	$C_{10}C_{17}C_{11}$	124.5 (5)
N_3FeN_4	90.2 (2)	$N_1C_9C_1$	109.3 (5)	$C_{12}C_{24}C_{13}$	122.6 (5)
N_3FeN_{a1}	88.5 (2)	$N_1C_9C_{38}$	126.9 (5)	$C_{14}C_{31}C_{15}$	123.4 (5)
N_3FeN_{b1}	92.3 (2)	$C_1C_9C_{38}$	123.7 (5)	$C_9C_{38}C_{16}$	121.8 (5)
N_4FeN_{a1}	88.0 (2)	$N_1C_{10}C_2$	109.6 (5)	$FeN_{a1}C_{a1}$	125.5 (4)
N_4FeN_{b1}	89.8 (2)	$N_1C_{10}C_{17}$	125.5 (5)	$FeN_{a1}C_{a3}$	127.7 (4)
FeN_1C_9	126.8 (4)	$C_2C_{10}C_{17}$	124.6 (5)	$C_{a1}N_{a1}C_{a3}$	106.7 (5)
FeN_1C_{10}	126.8 (4)	$N_2C_{11}C_3$	109.6 (5)	$C_{a1}N_{a2}C_{a2}$	106.3 (6)
$C_9N_1C_{10}$	106.3 (4)	$N_2C_{11}C_{17}$	125.6 (5)	$N_{a1}C_{a1}N_{a2}$	111.7 (6)
FeN_2C_{11}	126.8 (4)	$C_3C_{11}C_{17}$	124.8 (5)	$N_{a2}C_{a2}C_{a3}$	107.5 (6)
FeN_2C_{12}	127.3 (3)	$N_2C_{12}C_4$	110.2 (5)	$N_{a1}C_{a3}C_{a2}$	107.9 (6)
$C_{11}N_2C_{12}$	105.8 (4)	$N_2C_{12}C_{24}$	125.7 (5)	$FeN_{b1}C_{b1}$	126.0 (4)
FeN_3C_{13}	127.2 (4)	$C_4C_{12}C_{24}$	124.0 (5)	$FeN_{b1}C_{b3}$	127.7 (4)
FeN_3C_{14}	125.8 (4)	$N_3C_{13}C_5$	109.9 (5)	$C_{b1}N_{b1}C_{b3}$	106.1 (5)
$C_{13}N_3C_{14}$	106.5 (4)	$N_3C_{13}C_{24}$	126.7 (5)	$C_{b1}N_{b2}C_{b2}$	107.9 (5)
FeN_4C_{15}	127.0 (4)	$C_5C_{13}C_{24}$	123.3 (5)	$N_{b1}C_{b1}N_{b2}$	110.1 (6)
FeN_4C_{16}	127.2 (4)	$N_3C_{14}C_6$	108.9 (5)	$N_{b2}C_{b2}C_{b3}$	107.0 (6)
$C_{15}N_4C_{16}$	105.8 (4)	$N_3C_{14}C_{31}$	126.2 (5)	$N_{b1}C_{b3}C_{b2}$	108.9 (6)
$C_2C_1C_9$	107.4 (5)	$C_6C_{14}C_{31}$	124.8 (5)		

[a] Numbers in parentheses are the estimated standard deviations.

Table V. Selected Bond Parameters Associated with the Phenyl Groups and the Methanol of Solvation[a,b]

Type	Length, Å	Type	Length, Å	Type	Length, Å
$C_{17}-C_{18}$	1.515 (8)	$C_{26}-C_{27}$	1.41 (1)	$C_{36}-C_{37}$	1.40 (1)
$C_{18}-C_{19}$	1.39 (1)	$C_{27}-C_{28}$	1.37 (1)	$C_{38}-C_{39}$	1.499 (8)
$C_{18}-C_{23}$	1.37 (1)	$C_{28}-C_{29}$	1.38 (1)	$C_{39}-C_{40}$	1.38 (1)
$C_{19}-C_{20}$	1.40 (1)	$C_{29}-C_{30}$	1.38 (1)	$C_{39}-C_{44}$	1.38 (1)
$C_{20}-C_{21}$	1.37 (1)	$C_{31}-C_{32}$	1.492 (8)	$C_{40}-C_{41}$	1.38 (1)
$C_{21}-C_{22}$	1.36 (1)	$C_{32}-C_{33}$	1.37 (1)	$C_{41}-C_{42}$	1.37 (1)
$C_{22}-C_{23}$	1.41 (1)	$C_{32}-C_{37}$	1.39 (1)	$C_{42}-C_{43}$	1.37 (1)
$C_{24}-C_{25}$	1.486 (8)	$C_{33}-C_{34}$	1.38 (1)	$C_{43}-C_{44}$	1.38 (1)
$C_{25}-C_{26}$	1.38 (1)	$C_{34}-C_{35}$	1.34 (1)	O_m-C_m	1.40 (1)
$C_{25}-C_{30}$	1.38 (1)	$C_{35}-C_{36}$	1.38 (2)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant figures. [b] The sum of the three bond angles subtended at each methine carbon atom (C_{17}, C_{24}, C_{31}, C_{38}) is 360.0°; the interior angles of every phenyl group average to 120.0°, with no significant deviation from the mean.

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(28) M. J. Hamor, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, **86**, 1938 (1964).

(29) E. B. Fleischer, C. K. Miller, and L. E. Webb, *ibid.*, **86**, 2342 (1964).

square value of the estimated standard deviations for the several independently determined distances. The observed distance corresponds to σ bonding between a pair of trigonally hybridized carbon atoms.

Bond lengths in the porphinato core of the $(Im_2FeTPP)^+$ cation also conform rather well to a pattern of fourfold symmetry. Using C_a and C_b to denote the respective α- and β-carbon atoms of the pyrrole rings, and C_m for methine carbon, averaged lengths for chemically analogous bonds are: N–C_a, 1.378 (8, 7); C_a–C_m, 1.392 (9, 8); C_a–C_b, 1.437 (8, 8); C_b–C_b, 1.350 (7, 9) Å. It is evident that in every case the mean deviation from the average differs insignificantly from the root-mean-square (rms) estimated standard deviation of an individual datum.

The averaged length, 1.381 (12, 11) Å, of the 24 C–C bonds in the peripheral phenyl groups displays the apparent shortening from the standard internuclear separation of 1.397 Å that is largely attributable to the complex, strongly excited, thermal motions of the peripheral groups.

The aromatic character of the N–C and C–C bonds in the imidazole rings is evident in the bond lengths (Table III) that are displayed on the diagram in Figure 1. With the possible exception of the N_{a2}–C_{a2} and N_{b2}–C_{b2} bonds, which differ in length by an apparent 0.033 Å, structural quasi equivalence of the two rings is indicated. A significant departure from equivalent complexing of the two imidazole molecules, attributable to difficult packing relations in the crystal, is discussed below.

In marked contrast with cobalt(III), neither the isoelectronic iron(II) nor iron(III) ordinarily form low-spin complexes with nitrogen of exclusively monodentate ligands. Iron–nitrogen bond lengths for such octahedral covalent bonding are predicted[30] to differ by only ~0.02 Å for chemically analogous Fe(II) and Fe(III) complexes with a mean value that differs insignificantly from the cobalt–nitrogen bond length in the analogous low-spin Co(III) species. Consequently, a useful datum for reference in discussing the low-spin iron porphyrins of this and the accompanying paper[10] is the averaged Co–N bond length, 1.955 ± 0.015 Å,[31] from structure determinations for low-spin cobalt(III) complexes in each of which the central atom is bonded to nitrogen atoms of six monodentate ligands. This value is appreciably larger than the 1.92 Å given by the sum of the octahedral covalent radii[31] and observed in the low-spin ethylenediaminetetraacetatocobaltate(III) ion.[32]

The averaged length of the four complexing bonds to porphinato nitrogen atoms in the $(Im_2FeTPP)^+$ cation is Fe–N = 1.989 (5, 4) Å; departures of the complex from effective fourfold symmetry are reflected in the rather small (0.005 Å) mean deviation from the average. That this bond length should be significantly

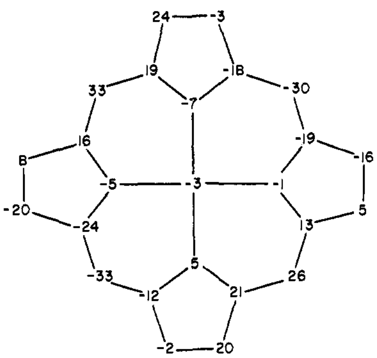

Figure 3. Diagram to illustrate the quasi-S_4 ruffling of the porphinato core of the $[Im_2FeTPP]^+$ cation. The perpendicular displacements of the atoms from the mean plane, in units of 0.01 Å, replace the symbols of these atoms as carried on the identically oriented diagram of Figure 1.

larger than the ~1.95 Å anticipated with six monodentate ligands is quite in agreement with earlier analysis of the structural properties of the porphinato skeleton.[3,5,23] Radial strain in the plane of the porphinato skeleton of a metalloporphyrin appears to be minimized for a "radius of the central hole," Ct···N,[33] of ~2.01 Å, and the skeleton strongly resists undue radial extension or contraction,[23] especially the latter. Thus, a length of 1.99 Å for the complexing bonds corresponds to relatively little radial strain in the porphinato skeleton of the $(Im_2FeTPP)^+$ complex.

Complexing bond lengths to imidazole A, 1.957 (4) Å, and imidazole B, 1.991 (5) Å, as observed in the crystal, differ significantly. A small out-of-plane displacement of the iron atom, 0.009 (3) Å, toward the more distant imidazole B suggests that the bond to imidazole A is slightly stretched, and that the length of this bond in the unconstrained $(Im_2FeTPP)^+$ cation probably does not exceed 1.95 Å. Although we can envision an electronic structure for the unconstrained paramagnetic (S = $^1/_2$) complex whereby nonequivalence of the axial bonds would be required, it is advisable first to examine the steric interactions of the porphinato core with the neighboring pair of hydrogen atoms on each imidazole ring (Figure 2) as a function of the orientation of the imidazole around the complexing axial bond. This is conveniently done with the aid of Figure 4 in which the traces of the flat imidazole ligands on the mean plane of the porphinato core are displayed.

The steric relations are illuminated by initial consideration of an idealized model in which the complexing bond to the imidazole nitrogen atom (N_{Im}) is taken to be a dimensionally exact twofold axis normal to a porphinato core of effectively D_{4h} symmetry. The dihedral angle (ϕ) between the plane of the imidazole and a plane defined by the N_1, N_3, and N_{Im} positions (Figure 4) specifies the orientation of the ligand. Upon rotation of this (internally averaged) ligand around the Fe–N_{Im} bond, the two hydrogen atoms (H_{Im}) contiguous to the N_{Im} atom (Figure 2) describe a circle of ~2.07 Å radius (Figure 4). Minimum steric interaction, requiring $\phi = \pm 45°$, puts each H_{Im} atom above a six-membered

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(30) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(31) N. E. Kime and J. A. Ibers, *Acta Crystallogr., Sect. B*, 25, 168 (1969); F. A. Cotton and W. T. Edwards, *ibid., Sect. B*, 24, 474 (1968). Averaged Co–N distances from different complexes lie in the range 1.94–1.97 Å.

(32) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, 81, 550 (1959). Whereas the Co–O and Co–N bond lengths differ by only ~0.04 Å, the van der Waals packing diameters of oxygen and nitrogen differ by ~0.20 Å. Consequently, the very tight ligand packing that characterizes a CoN_6 coordination group is eased by the substitution of oxygen for two-thirds of the nitrogen atoms.

(33) Centering (at Ct) of the metal atom (M) among the porphinato nitrogen atoms makes M–N≡Ct···N; the Ct···N radius retains its special significance for the analysis of radial strain whenever the metal atom is substantially displaced out-of-plane, as in the zinc and high-spin iron porphyrins.[5,21,23]

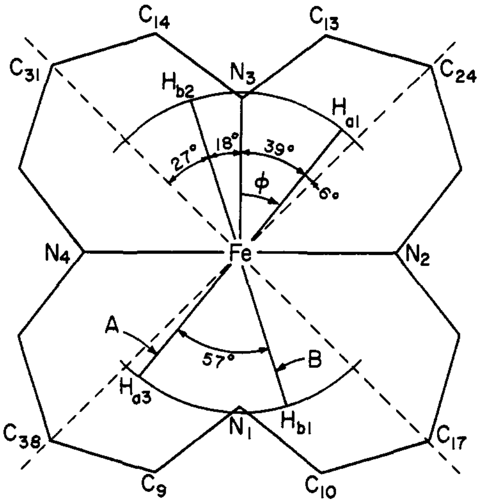

Figure 4. Slightly idealized diagram (see text) showing the traces on the basal plane of the planar imidazole ligands A and B. The circle (represented by the two arcs) that passes so very near to the positions of the porphinato nitrogen atoms is the projection on the basal plane of the motion described by the pair of hydrogen atoms contiguous to the complexed nitrogen atom upon rotation of an imidazole ligand around the axial Fe–N bond. Atoms H_{a1}, H_{a3}, H_{b1}, and H_{b2} of this diagram are attached to the respective carbon atoms C_{a1}, C_{a3}, C_{b3}, and C_{b1} of Figure 1 and Table I.

chelate ring roughly equidistant from a C_m carbon, two C_a carbon, and two (N_p) nitrogen atoms of the core; the respective separations, with Fe–N_{Im} = 1.95 Å, are calculated to be 2.78, 2.81, and 2.88 Å. Maximum steric interaction, with ϕ = 0 or 90°, places H_{Im} and N_p atoms in almost direct superposition; their calculated separation, with Fe–N_{Im} = 1.95 Å, is only 2.43 Å, whereas the normal packing distance for this geometry is ~2.90 Å, the sum of the van der Waals radii for hydrogen (1.20 Å) and aromatic nitrogen (1.70 Å). Thus for ϕ near 0 or 90°, a substantial stretching of the Fe–N_{Im} bond is in order.

Employing now the observed stereochemical parameters, the $H_{Im}\cdots N_p$ separations in imidazole A ($H_{a3}\cdots N_1$ and $H_{a1}\cdots N_3$) remain sensibly equal at ~2.79 Å. The $H_{a3}\cdots C_9$ and $H_{a1}\cdots C_{13}$ distances (Figure 4) are substantially longer, 2.90–2.94 Å, owing to the quasi-S_4 ruffling of the porphinato core. For imidazole B, by contrast, the $H_{b2}\cdots N_3$ and $H_{b1}\cdots N_1$ separations remain unduly tight at ~2.56–2.58 Å despite the stretching of the complexing bond to 1.99 Å. The easing of the $H_{b2}\cdots C_{14}$ and $H_{b1}\cdots C_{10}$ contacts to values >2.80 Å correlates again with the ruffling of the core. A large part, if not all, of the ruffling probably is required by the steric interactions.

Were we dealing with the chemically analogous, electrically neutral, iron(II) species—the diamagnetic Im_2FeTPP—the electronic and stereochemical equivalence of the axial ligands in the unconstrained molecule would scarcely be subject to doubt. Nor would this equivalence be disturbed upon abstraction of an electron from the iron $3d_{xy}$ orbital (lobes diagonally oriented relative to the four nitrogen atoms in the porphinato core) to give an $(Im_2FeTPP)^+$ cation. The abstraction, by contrast, of an electron from one of the d_{yz} or d_{zx} orbitals could give rise to a static Jahn–Teller effect operable on the back π bonding from the iron atom to the porphinato core and the axial ligands. Whether the concomitant restriction on the molecular symmetry would be accompanied by objectively significant variations in bond lengths that could be unambiguously attributed to differences in π bonding is doubtful at best. An Fe–N_{Im} bond length of 1.95 Å might be taken to imply some contribution from back π bonding.

The octahedral coordination groups in the $[Im_2FeTPP]^+$ ion, the Pip_2FeTPP molecule of the accompanying paper,[10] and the bis(dimethylglyoximato)diimidazoleiron(II) molecule[34] [written $Im_2Fe(DMG)_2$] all approximate dimensionally to tetragonal symmetry. Equatorial Fe–N bond lengths in these low-spin complexes are more strongly dependent upon the constraints imposed by the chelating ligands than upon the oxidation state of the iron atom. With the Fe(II) atom held in the vise-like grip of the bis(DMG) ligand system,[34] the equatorial Fe–N bond lengths average to only 1.905 (13, 6) Å, a good deal shorter than the ~1.97 Å anticipated for iron(II) with six monodentate nitrogen ligands (*vide supra*). The stretched equatorial Fe–N distances in the $[Im_2FeTPP]^+$ and Pip_2FeTPP species, 1.989 (5, 4) and 2.004 (4, 3) Å, respectively, do reflect the differing oxidation states of the iron atom, although the difference in bond lengths is held to a minimum by the pronounced resistance of the porphinato core to undue contraction. Bowman, *et al.*,[34] point out that the axial imidazole ligands in the centrosymmetric $Im_2Fe(DMG)_2$ molecule are well oriented to minimize steric repulsions and, consequently, that the longer axial Fe–N bond of 1.985 (5) Å in this species, as compared with the 1.957 (4) Å to imidazole A in the $[Im_2FeTPP]^+$ ion, is attributable to the difference in oxidation state of the iron atom. We concur in this conclusion; we add only that the extraordinarily tight packing of the nitrogen atoms in the girdle of the $Im_2Fe(DMG)_2$ molecule may require a small lengthening of the axial bonds beyond the value best representative of low-spin iron(II) with six monodentate nitrogen ligands.

The incapacity of the piperidine molecule to accept electron density by back π bonding from the iron atom may contribute, in some measure, to the much longer axial bonds, 2.127 (3) Å, observed in the centrosymmetric Pip_2FeTPP molecule; it is entirely clear, however, that unavoidable steric interactions similar to, but much more serious than, those involving imidazole B in the $[Im_2FeTPP]^+$ ion bear the principal responsibility.[10]

The chloride ion is positioned in the crystalline arrangement so as to be rather strongly hydrogen bonded to the uncomplexed nitrogen atom of an imidazole molecule of type B, and rather less strongly hydrogen bonded to the hydroxyl group of the methanol molecule. The Cl···N distance is 3.07 Å, and the N–H bond points nearly at the chloride ion to give a calculated Cl···H distance of ~2.13 Å. The Cl···O separation is 3.16 Å, and the O–H bond presumably can be directed toward the chloride ion because the angle ClOC is 111°. Although the oxygen atom of this methanol molecule lies 2.90 Å from an uncomplexed nitrogen atom of an imidazole ligand of type A in a second complex cation, the N–H bond is not well directed for strong hydrogen bonding: the calculated O···H separation of ~2.31 Å is significantly longer than the Cl···H distance of 2.13 Å that involves the much bulkier chloride ion.

(34) K. Bowman, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, **94**, 727 (1972).